Application of analytical pyrolysis to the characterization of *Eucalyptus* extractives and pitch deposits from a pulp mill

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Abstract

It has been demonstrated that both conventional flash pyrolysis and thermally assisted hydrolysis and alkylation (THA) in the presence of tetramethylammonium hydroxide (TMAH), enable the detection of some important components of wood extractives (WE) from *Eucalyptus globulus*. These are released by thermoevaporation from the acetone extracts and easily identified by GC-MS. On the other hand, Py-GC-MS with and without TMAH has proven to be a very useful technique for a rapid characterization of pitch deposits both from the machine area and from TCF end-pulp from *E. globulus*. In spite of the low ratio analyte/matrix in the second case, the pyrograms from the pitch-enriched pulp samples showed a satisfactory reproducibility, and some significative pyrolysis compounds arising exclusively from the pitch deposit were also evident, although their specific origin could not be unambiguously determined.

Keywords: Analytical pyrolysis; Wood extractives; Pitch deposits; *Eucalyptus globulus*

1. Introduction

The technical significance of wood extractives (WE) to the pulp and paper industries has deserved much attention from decades and continues to be of great interest [1,2]. WE—a term which refers to the large and diverse mixture of wood components which are soluble in organic solvents [3]—interfere with the pulping process, and are responsible, besides the additives entering the system, of pitch trouble, which has important commercial implications, among other effects, of adversely affecting the quality of finished pulp.

The current analysis of all WE requires the use of tedious fractionation procedures of the global extracts prior to the separation and identification of components by GC-MS [4,5]. The possibilities of pyrolysis gas chromatography mass spectrometry (Py-GC-MS) for fingerprint differentiation between WE from soft- and hardwoods have been recently pointed out by Hardell [6]. However, its potential application to the qualitative and quantitative characterization of WE has not been exploited yet. As a prerequirement for this application, it is necessary the use of pyrolytic conditions under which relatively few secondary reactions are allowed; as it occurs with the open pyrolysis systems with fast heating rates and rapid removal of the pyrolysis products [7]. Besides, the major components of the mixture should evaporate before pyrolysis or give a suite of diagnostic pyrolysis compounds that would enable their indirect identification. Previous studies with model compounds have discussed the mechanisms of the dissociation processes by which thermoevaporated compounds are generated [8]. This thermal behaviour has been observed by Gelin et al. [9] even with functionalized high-molecular weight lipids.

On the other hand, Py-GC-MS has proven to be a very useful technique for the analysis of polymers in industrial depositions, including the large variety of impurities described in the paper pulp production processes, generically denominated pitch deposits ([2,6,10], and references therein).

In order to take corrective actions for pitch depositions, it is necessary to determine their composition, which usually consists of an intractable mixture from various origins, including wood extractives and the numerous solvent soluble additives (oils from defoamers and lubricants, sizing and coating agents, etc.) entering the system. Although pitch problems are very common in softwood pulping and papermaking processes, they are also of great economic relevance in the production of high quality hardwood chemical pulps, particularly from *Eucalyptus*, a species extensively used for paper pulp manufacture in Spain and Portugal.

With the above considerations in mind, the present work has two different aims. The first is to apply conventional Py-GC-MS and thermally assisted hydrolysis and alkylation (THA) in the presence of tetramethylammonium hydroxide (TMAH) for the qualitative characterization of WE from *Eucalyptus globulus*. The second focuses on the characterization by pyrolytic and non-destructive spectroscopic techniques (FT-IR and CPMAS NMR) of two different pitch deposits collected from the machine area of an *Eucalyptus* pulp mill and from the TCF end pulpsheets, aiming to identify the origin and/or nature of these impurities.

2. Experimental

Freeze-dried samples of *Eucalyptus globulus* chips were weighed into extraction thimbles and Sohxlet extracted with HPLC grade acetone. The average yield of *Eucalyptus* wood extractives (EWE) amounted to 1.1%. Two pitch samples were provided by ENCE pulp mill (Pontevedra, Spain). One corresponds to deposits collected from the machine area (one of the presses in the mill's drying section), and the second one was collected from end pulp plates (marked pulp) using tweezers under a dissecting microscope and separated from fibres as far as possible.

The FT-IR spectra of the pitch deposits were obtained with a Nicolet 510 Nic-Plan spectrometer by co-adding 100 scans at a resolution of 2 cm^{-1}.

The solid state ^{13}C CPMAS NMR spectra were obtained with a Bruker MSL-300 at a frequency of 74.5 MHz at a magic angle rotation rate of 4 kHz with a contact time of 1 ms, and pulse delay of 300 ms after accumulation of 25 000 transients. Details of the experimental procedure have been previously reported [11].

Pyrograms from the crude acetone extracts (EWE), the pulp as such and the pitch deposits were recorded under the same analytical conditions with and without alkylating reagent. In the first case the samples were dissolved in the minimum amount of TMAH in 25% aqueous solutions (Aldrich) and dried in an air-evacuated desiccator overnight. The syrups were placed on the ribbon foil of the CDS pyroprobe and heated to 500°C for 10 s. For conventional pyrolysis without alkylating reagent the samples were placed in quartz tubes. Chromatographic separation of the pyrolysis products was achieved employing a fused silica column (SE-52, J&W Scientific) of 25 m length and 0.2 mm I.D. The gas chromatograph (Hewlett Packard HP-5890) was programmed from 40 to 300°C at a rate of 6°C min^{-1}. Helium (1 ml min^{-1} flow rate) was used as carrier gas. The mass spectrometer (HP 5988 A) was set at 70 eV. Identification was achieved by mass fragmentography, library search and comparison with literature data.

3. Results and discussion

The solid state NMR spectrum of the EWE (Fig. 1) shows the great complexity of the mixture of *Eucalyptus* extractives present in the crude acetone extract. Thus, C atoms from aromatic and unsaturated compounds (110–160 ppm) coexist with

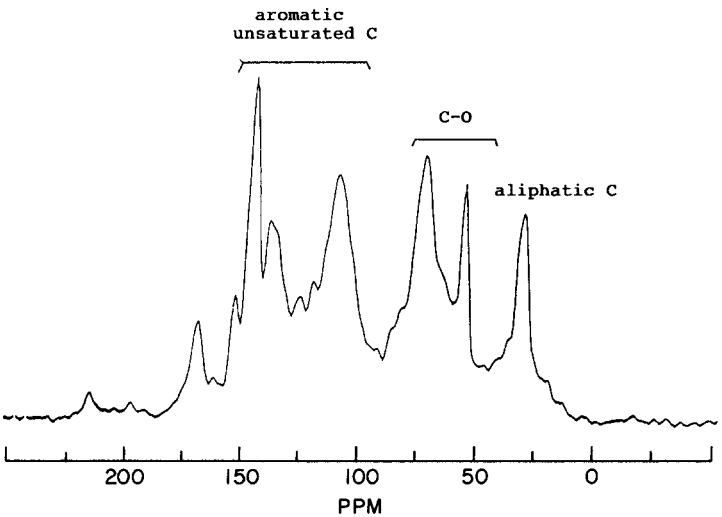

Fig. 1. CPMAS NMR spectrum of a crude *Eucalyptus* acetone extract.

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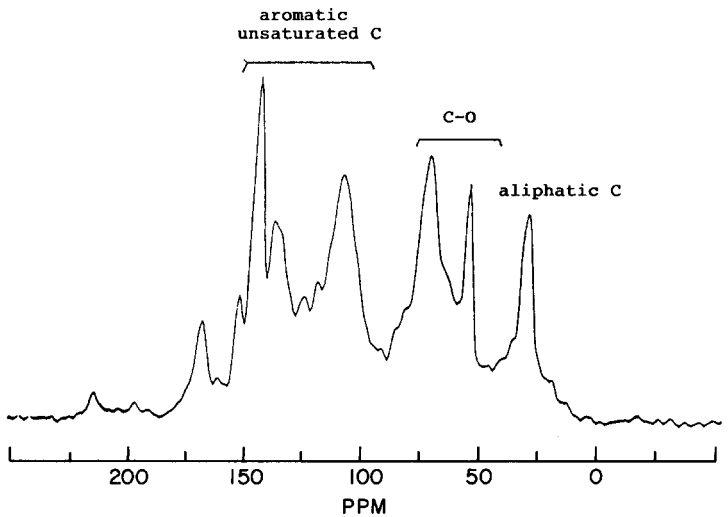

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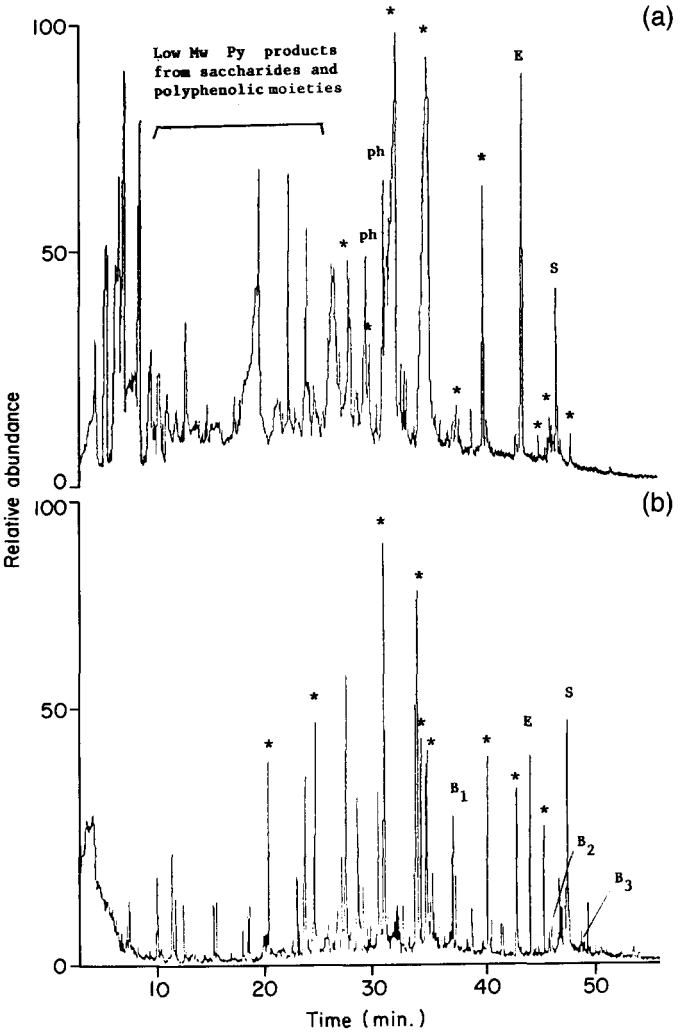

Fig. 2. Pyrograms in absence (a) and presence (b) of TMAH of *Eucalyptus* wood extractives. E, squalene; Ph, dialkyl phthalates; S, β-sitosterol; B1, B2, B3, biomarkers of *Eucalyptus globulus*.

aliphatic (0–30 ppm) and C–O substituted (40–90 ppm) structures and functional groups (170–200 ppm).

The pyrograms of the acetone-extracts with and without TMAH shown in Fig. 2 are also very complex. Most of the peaks both of aliphatic and aromatic nature arose from the pyrolysis of the saccharide and polyphenolic moieties, which constitutes an important part of the *Eucalyptus* acetone extracts [12,13]. Many methylated counterparts were also easily identified when using the THA procedure.

Both profiles also displayed distinctive compounds previously identified as *Eucalyptus* extractives, which have been marked on the corresponding peaks with asterisks. These consist of β-sitosterol (peak S) and fatty acids, which occurred both free and esterified with glycerol (mono-, di- and triglycerides) and sterols (steryl esters). The pattern of saturated (ions at *m/e* 74) and unsaturated (at *m/e* 67) fatty acids (Fig. 3) extracted from the THA pyrogram (Fig. 2b) was coincident with that identified by fractionation procedures [unpublished results]. The above compounds seem, therefore, to be released by simple evaporation from the EWE mixture during pyrolysis.

Other components of the *Eucalyptus* extractives could also be recognized by the formation of suites of highly specific pyrolysis products, such as the steryl esters. Thus, peaks showing typical fragmentation patterns of steryl esters with steroid nucleus of sitostand (*m/e* 398), sitosterol (*m/e* 396) and fucosterol (*m/e* 394) were identified [14]. It is also probable that other neutral high molecular weight components from *Eucalyptus* extractives suffered transfer problems from the pyrolysis unit to the GC column and could not be analyzed either as pyrolysate or as evaporate.

It is also interesting to note the identification of some pyrolysis compounds, not yet described among the WE from *Eucalyptus globulus*, such as two alkaloids (peak B1, Fig. 2a: $C_{21}H_{22}N_2O_2$, Mw: 334 and peak B2: $C_{22}H_{26}N_4$, Mw: 346), and α-tocopherol (peak B3). These compounds are biologically active secondary metabolites and can be considered as 'biomarkers' of this *Eucalyptus* species according to the terminology used by Challinor [15].

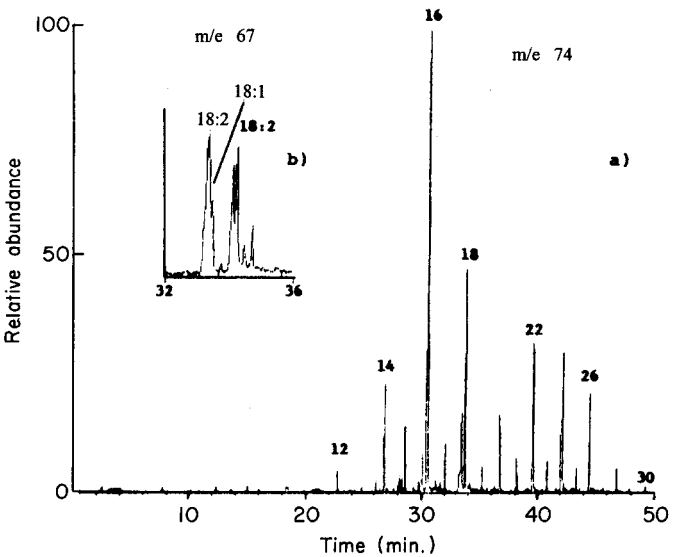

Fig. 3. Traces of saturated (a) and unsaturated (b) *n*-fatty acids methyl esters from the EWE pyrogram.

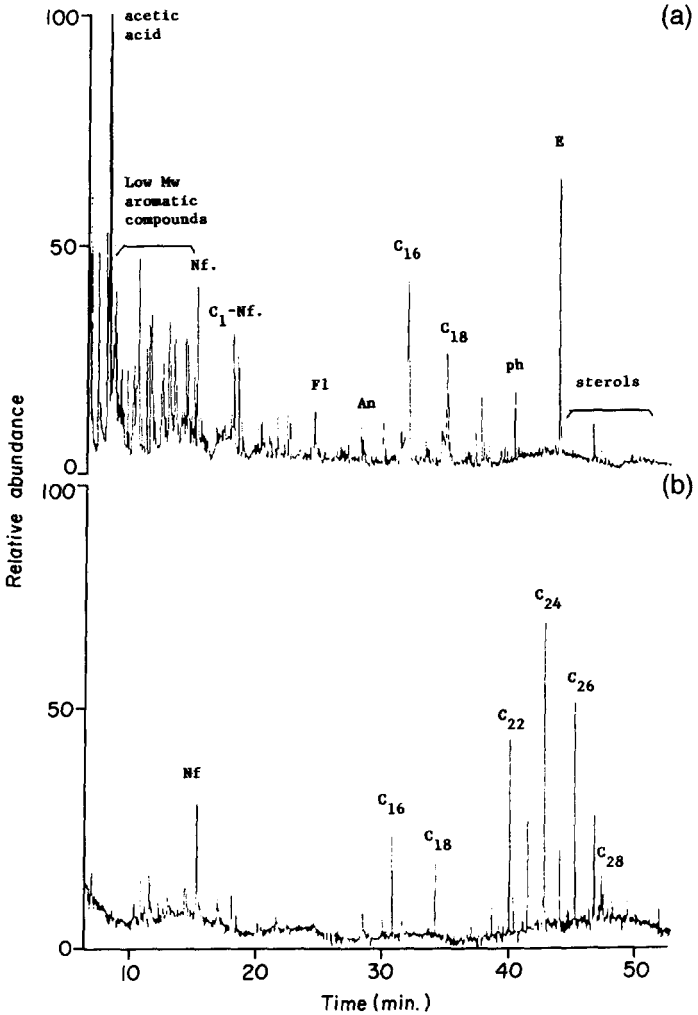

Fig. 4. Pyrogram of a pitch deposit from the machine area without (a) and with TMAH (b).

The pitch deposit collected from the machine area of the *Eucalyptus* pulp mill seemed to be a complex mixture displaying featureless CPMAS NMR and FT-IR spectra (not shown here). Fig. 4 shows the pyrogram of this deposit with (Fig. 4b) and without TMAH (Fig. 4a). The latter showed great diversity of aromatic and unsaturated structures and low Mw meaningless thermal fragments, which could not be adscribed to a specific origin. However, thermoevaporated fatty acids (Fig. 4b) had a different pattern to that corresponding to the wood resins (Fig. 3).

Py-GC-MS has proven to be useful for the analysis of those pitch deposits that occur in very low amounts [6], such as spots in pulp sheets, the second pitch sample

studied. Due to the low ratio analyte/matrix, the spectroscopic techniques enabled only very little differentiation between the samples of pure pulp and pitch-enriched pulp, as it is apparent from the comparison of the FTIR and CPMAS NMR

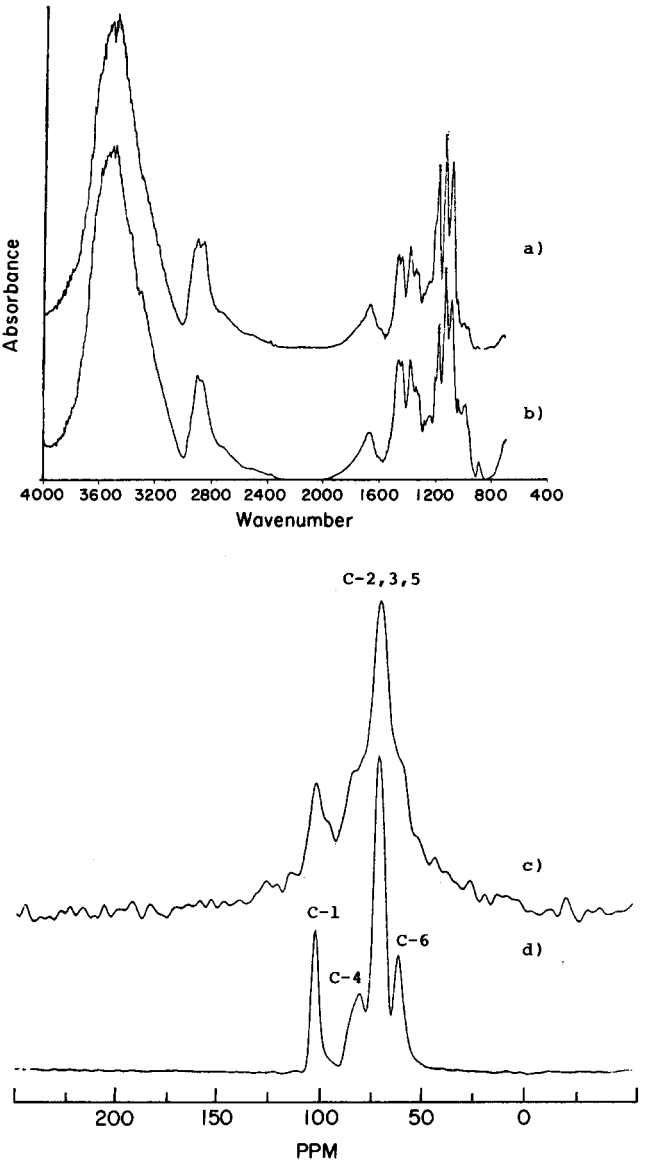

Fig. 5. FT-IR and CPMAS NMR spectra of reference pulp (a, c) and spots present in the pulpsheets (b, d).

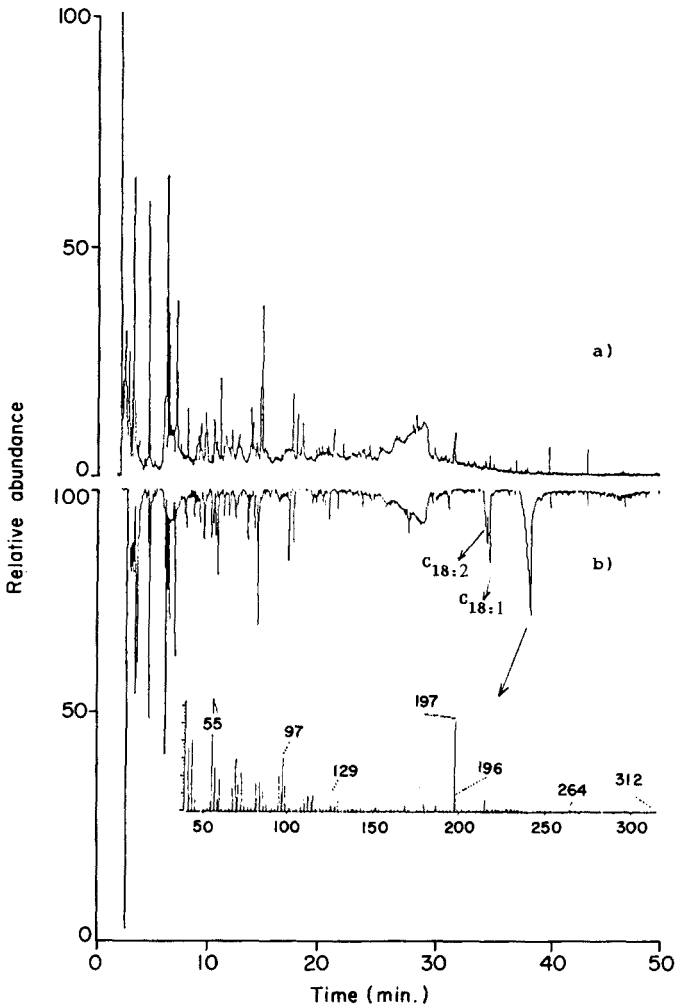

Fig. 6. Pyrograms of the reference pulp (a) and of spots present in end pulpsheets (b).

spectra shown in Fig. 5. Thus, both the FTIR spectrum of the pure pulp (Fig. 5a) and the spots (Fig. 5b) shows the same typical carbohydrate bands at about 1080, 1130, 1180 and 1660 cm^{-1}, with only quantitative differentiations between them. Regarding the solid-state NMR spectra (Fig. 5c, d) the spot enriched pulp spectrum shows no distictive bands, although the typical bands of kraft pulp [16] are less resolved.

The pyrograms from the analysis of pure pulp and pitch in pulp are shown in Fig. 6. In spite of the great amount of fibre material contained in the isolated pitch, the pyrolytic techniques enabled the identification of specific pitch components. Thus, performing a fingerprint comparison of both pyrograms, it is evident that the

first parts are practically identical, being identified the typical compounds arising from the pyrolysis of pure pulps previously described [17]. However, three pyrolysis compounds were only clearly present in the pyrogram of the pitch-enriched sample. Two of them were identified as the unsaturated *n*-fatty acids C18:1 and C18:2, very abundant in the *Eucalyptus* extractives, and the third one showed the mass spectrum included in Fig. 5., which had no matches in the usual libraries (Wiley, Nist), and seemed to correspond to a functionalized branched oleic moiety.

4. Conclusions

Some significative components of *Eucalyptus* extractives were unambigously identified in flash pyrolysates of acetone extracts, whereas other could be recognized by the formation of suites of highly specific pyrolysis products. The rapid characterization of WE allowed by pyrolytic techniques can be very important when a routine determination of WE is needed. It is most probable that the optimization of the pyrolysis conditions and chromatographic column performance could lead to soon improve the characterization of WE by Py-GC-MS.

Likewise, Py-GC-MS both with and without TMAH has proven to be a very useful technique for the rapid characterization of pulp impurities (pitch deposits present in minute amounts) on TCF end pulp from *E. globulus*. In spite of the low ratio analyte/matrix, the reproducibility of the pitch containing samples pyrograms was high and some significant differentiation was evident. However, the identification of some pyrolysis compounds arising exclusively from the pitch depositions could not be unambiguously used for determinations of their origin.

Acknowledgements

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